INVESTIGATION ON THE RELEASE KINETICS OF CHROME FROM FINISHED CHROME TANNED LEATHER

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Abstract: Chrome tanning is the commonest tannage in leather manufacture, and the discard of chrome tanned leather goods inevitably leads to chrome release that might have potential environmental risks. In this study, the kinetic behaviors of the release of chrome were investigated by ICP-OES. Deionized water was used as medium and the parameters such as liquid/solid ratio, pH, contact time, temperature and rotational speed affected leaching behavior of chromium in the finished chrome-tanned leather shavings were studied. Then, the leaching tests were proceed at solid liquid ratio 1:20 as well as rotational speed 60 r/min to simulate the release of chrome tanned leather under natural conditions. The effect of temperature on the kinetics behavior was further explored. The results showed that the release of chrome could be well fitted by weber–morris model and the second-order kinetic equation, and two type of process controlled the rate of the release of chrome. Though the release of chrome is lasting, more than 85% leachable chrome in leather could be released in 24 h. The results could provide the theoretical parameters for the assessment of risks of chrome-tanned leather.

1 Introduction

Tanning is a important process procedure to converts animal hides or skins into leather[1, 2]. It's a resource utilization for recycling an organic waste from the meat industry and creates valuable products, such as footwear, that meet consumer's requirements in terms of comfort and fashion[3, 4]. There are many kinds of tanning methods, including metal salts, aldehyde derivatives, syntans, vegetable tannins and their combination tannages[5-7]. Because of the uniqueness properties that Cr-tanning leather confers to the resulting products[8], it accounts for more than 80% of the tannages in the past 20 years[9].

During the production of chrome-tanned leather, the chromium incorporated into the collagen fiber with at least three types of interactions, including that chromium is complexed with collagen, non-productive binding of chromium to collagen(chromium be bound to the collagen, but no crosslinked) and adsorption of chromium by the collagen matrix. The different interactions lead to different binding ability for chromium to collagen. Not more than 1.5% of the total chromium been adsorbed by the collagen matrix that could be removed easily. Nearly 58.5% of the total chromium is complexed with collagen, it has great effect on the thermal stability of chromium-collagen complex, and it is harder to removed. Nearly 40% of the total chromium is tightly bound to the collagen, but no crosslinked, that has no effect on thermal stability, and it is also harder to removed[10]. When the leather goods become waste at the end of their life span, the chemicals in leather especial chromium can be leached out to pollute surface water, soil or even underground water by surface rain's leaching procedure. The migration rule may be related to the interactions of chromium to collagen.

In this study, the deionized water was used as the leaching agent to simulate the leaching behavior of leather in surface water. Some parameters such as liquid/solid ratio, pH, contact time, temperature and rotational speed affected leaching behavior of chromium in the finished chrome-tanned leather shavings were studied and the leaching kinetics of chrome tanned leather was further studied.

2 Materials and Methods

2.1 Materials and Analysis

The finished chrome tanned leathers obtained from different tannery were used in the present study. The sample was shredded to ≤4 mm (using a Retsch mill with rotating knives and a 4 mm sieve), and thoroughly homogenized and conditioned in standard laboratory atmosphere (293.15 ± 2 K and 65 ± 5% relative humidity) for 48h. Deionized water was used as extractor fluid to evaluate the leaching behaviors of leather waste. All chemicals such as hydrochloric acid, nitric acid, sodium hydroxide and hydrogen peroxide were of analytical grade provided by Chengdu Jinshan Chemical Reagent Co Ltd. The standard solution of chrome was obtained from National Nonferrous Metals and Electronic Materials Analysis and Testing Center (Beijing, China), and inductively coupled plasma atomic emission spectrometry (ICP-AES, OPTIMA 8000) is used to detect the total chromium content in leaching solution.

2.2 Experimental Procedure

2.2.1 Determination of chrome content in finished chrome tanned leather

A weight of 1.0 g Cr-tanning powder was digested by microwave method. The procedure of microwave digestion[11] (Anton Paar Multiwave PRO, Austria) consisted of a 10-min gradual increase to 1400W, a 20-min digestion step at 1400W and then a cooling stage. The digestion solution was mixed thoroughly after adjusting to a constant total volume. The total chrome in leather was analyzed directly by inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000, USA).

2.2.2 Leaching experiments

Leaching experiments were conducted with air constant temperature shaker (ZWY-2102C, Shanghai China) with temperature precision of ±0.1℃. The leachates passing through 0.45μm membrane filters were digested by wet digestion method that using concentrated nitric acid and hydrogen peroxide (3:1, v/v). The digestion liquor was filtered and adjusting to a constant total volume with deionized water, and the concentration of chrome was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000, USA).The calibration standard (0.20-5.00mgL-1) was prepared by diluting the chrome standard stock solutions (100mg L-1). All the tests were done in duplicate.

The leaching experiments in this paper are mainly divided into two parts. First, the leaching conditions such as temperature varying from 20℃to 35℃,the shaker speed from 30rpm to 210rpm, liquid-solid ratio from 70:1 to 10:1, and pH of extractor from 2 to 11 are optimized continuously. The pH of extractor was adjusted by addition of 0.1mol.L^{-1} HCl or NaOH appropriately, and measured using FE20-Five Easy Plus™ pH meter, Mettler-Toledo.

Second, the leaching kinetics of chromium from Cr-tanned leather powder in aqueous solution was investigated in detail. This part of the leather is thinner than those used in previous experiments. The kinetic researches were conducted for four different temperature 20℃,25℃,30℃ and 35℃respectively. A weight of 4.0g Cr-tanning powder was taken in 250 ml conical flask, fully soaked using 80ml ultrapure water (resistivity ≥18.2MΩ-cm) to simulate surface water. Then the 18 flasks were kept in a shaker at fixed temperature with rotational speed of 60rpm. Take two flasks at 1h, 2h, 4h, 8h, 24h, 48h, 96h, 168h, and 240h respectively to analyze the total chrome of the leachates as the above.

3 Results and Discussion

3.1 The Total Chromium in Leather

After the chrome tanned leather was digested by the microwave digestion instrument, the total chromium content measured by ICP-OES were 21445.83mg/kg and 20672.50 mg/kg respectively for two kinds of Cr-tanned leather.

3.2 Leaching Behavior of the Chromium

The leaching experiments of finished chrome-tanned leather shavings (FCTLS) were carried out with various experimental parameters, including liquid-solid ratio(LSR), pH, contact time (CT), temperature(T), and rotational speed(RS). The extractive chrome content was calculated by the following equation.

$$C=C_0 \times A$$

Where C represents the extractive chrome content, C_0 represents the concentrations of leachate, A represents the liquid/solid ratio. The effects of these leaching parameters on chromium leaching efficiency were investigated, as illustrated in Fig. 1(a)–(e).

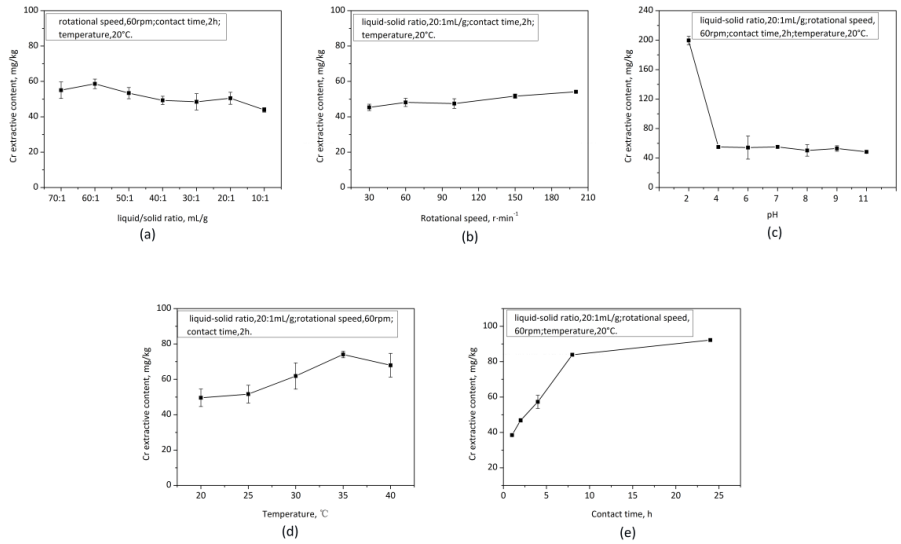

Fig. 1. The relation between Cr removal and leaching parameters:(a) liquid-solid ratio, (b) rotational speed (c)pH, , (d) temperature and (e) contact time.

The effect of liquid-solid ratio on chromium leach from the FCTLS was shown in Fig. 1(a). As presented, the leaching amount slightly decreased as the liquid-solid ratio decrease. However, considering the water absorption and swelling of leather powder, the liquid-solid ratio of 10:1 is not appropriate. The concentration of chromium released was in the range of 45.32-54.14mg/kg when changing the rotational speed of the shaker (Fig.1b), showing slight effect of rotational speed. In Fig. 1(c), the leachates of FCTLS contain a higher concentration of chromium, suggesting that the release of chromium from the FCTLS could be increased in an overly acidic environment. Whereas in the pH range of 4-11, the chromium concentration released was not significantly changed by the increase of pH value.

The contact time and temperature have greater influence on the extractive chrome content compared with liquid-solid ratio, rotational speed and pH of the fluid, as shown in Fig. 1d-e. The extractive content of Cr increases significantly with temperature. At 35°C, the extractive content of

Cr gets to the highest concentration. It indicated that the release of Cr was sensitive to the leaching temperature, the extractive content of Cr increased steadily as the contact time increased from 0 to 24 hours. At the first phase (1- 8 hours), the content of Cr increased rapidly with time. At the second phase (8-24hours), the change of Cr content was comparatively small. Then the effect of temperature and contact time were further investigated, whereas liquid-solid ratio and rotational speed were kept at 20:1 and 60rpm respectively, and deionized water was used as the fluid.

3.3 Kinetics Analysis for the Release of Cr

The release of chromium with respect to time was plotted in a graph shown as Fig. 1. From the figure, it is clear that the chromium release was temperature dependent. The chromium concentration was 0.21 mmol/L at 20℃ and 25℃, and 0.25 mmol/L at 30℃ and 35℃ for the shaking time 1 h respectively. However, appreciable change in the chromium concentrations at different temperature was achieved for the shaking times beyond 1 h especially at 35℃. With the increase of temperature, the total leached chromium increase. In the meantime, the leaching process becomes slower with time, and the leaching equilibrium didn't reached even after shaking 24h with replenished leaching solvent. In order to more fully understand the leaching mechanism, the kinetics on Cr release with different times at various temperatures were analyzed by using the shrinking core model, diffusion-based model and the homogeneous model, respectively.

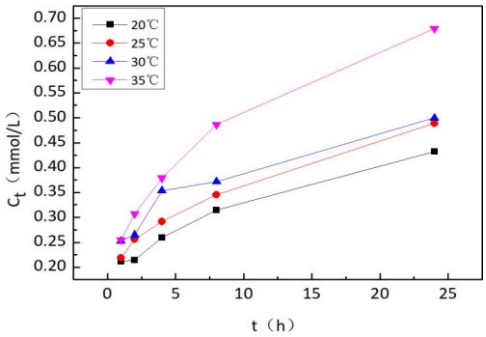

Fig. 2. Cr release at different temperature.

3.3.1 Shrinking core model (SCM)

This model was frequently used to describe the leaching reaction of the solid reactant with spherical particles. According to the model, the leaching reaction occurs first at the outer skin of the particle (ie. core) and moves into the solid, leaving behind completely converted material and inert solid (ie. shell). The model assumes the solid-liquid leaching reaction involves generally a chemical reaction on the surface of the core of unreacted reactants, accompanied by both fluid and solid phase (pore fluid) diffusion steps. Under the assumption of rate-control step, the shrinking core model could be simplified as the following equations[12-14].

For fluid film diffusion control:

$$x = k_1 t \qquad (1)$$

For pore diffusion control:

$$1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = k_2 t \qquad (2)$$

For chemical reaction control:

$$1 - (1 - x)^{\frac{1}{3}} = k_3 t \qquad (3)$$

where, k_i is the apparent constant for different control steps, x is the ratio of chromium content in liquid phase to total chromium content in dry leather powder (dimensionless), and t is the leaching time (h). Then the three equations were applied to test the control step of the Cr extracted by water. The plots were shown in Fig. 3 and the correlation coefficients were listed in Table 1.

Table. 1. Correlation coefficients (R^2) of various rate-control steps with the experimental data.

T/℃	Correlation coefficients(R^2) of three kinetic models		
	$x=k_1 t$	$1-3(1-x)^{2/3}+2(1-x)=k_2 t$	$1-(1-x)^{1/3}=k_3 t$
20	0.9516	0.9542	0.9543
25	0.9546	0.9579	0.9580
30	0.8687	0.8739	0.8741
35	0.9121	0.9193	0.9196

Just as shown in table 1, the correlation coefficient (R^2) values for these fitted curves are below 0.96. Taking into consideration of the geometrical factor of the powder of waste leather, which is a strip flake material with a loose and porous structure surface[15, 16], these three kinetic equations (1-3) were not suitable to demonstrate the leaching process of the scraps.

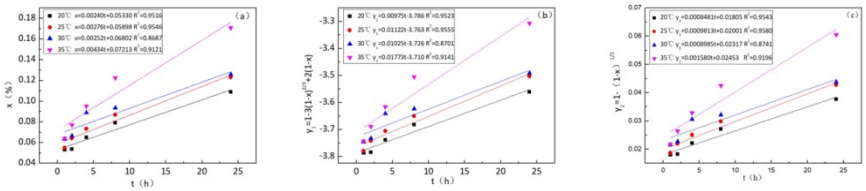

Fig. 3. Fitting of experimental data with fluid film diffusion control (a) and pore diffusion control (b) and chemical reaction control (c) of SCM.

3.3.2 Diffusion-controlled models

Weber–Morris model assumes that the mass transfer is the fast process, and only intraparticle diffusion is considered as rate-determining step. The kinetics equation is given as[17, 18]

$$C_t = k_w t^{0.5} + C \qquad (4)$$

where k_w denotes the rate constant of intraparticle diffusion determined by the slope of plot of C_t vs. $t^{0.5}$, and C represents the intercept. The graph of intraparticle diffusion model (Fig.4) showed linearity at all temperatures. The high values of R^2 suggested the applicability of intraparticle diffusion of Cr from the interstitial spaces and pores of the leather matrix to the fluid.

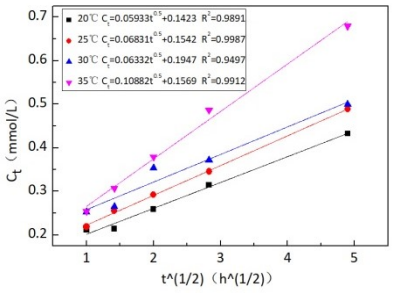

Fig. 4. Fitting of experimental data with Webber-Morris equation.

The deviation from the origin can be accounted by the fact that there is two type of process controlling the rate of the release of Cr.

3.3.3 Chemical kinetics-based model

Most of the reaction kinetics-based models consider the leaching process assuming that mass transfer is fast enough to be neglected. When the solid reactant is porous, the fluid reactant could freely diffuse into the interior of the solid. Then leaching could be considered as homogeneous reaction throughout the solid, and a gradual variation in the solid reactant concentration within the particle would appear during leaching process. Therefore, the experimental data were also applied to the pseudo-first-order kinetics and pseudo-second-order kinetics.

The equation for the pseudo-first-order kinetics can be expressed as[17, 18]:

$$\ln c_t = k_1 t + \ln C_s \qquad (5)$$

The general form of the pseudo-second-order kinetic model is written as[17, 18]:

$$\frac{t}{c_t} = \frac{1}{k_2 C_S^2} + \frac{t}{C_S} \qquad (6)$$

where c_t is the concentration of Cr in leachate in the time of t, and *Cs* is the concentration of chromium in leachate at the equilibrium state. while k_1 (h^{-1}) and k_2 (L $mmol^{-1}$ h^{-1}) are the rate constant of reaction respectively. The slope k_1 and 1/*C*s, as well as the intercept $\ln C_s$ and $1/k_2 Cs^2$ can be calculated by the linear fitting between the $\ln c_t$, t/c_t and t, respectively.

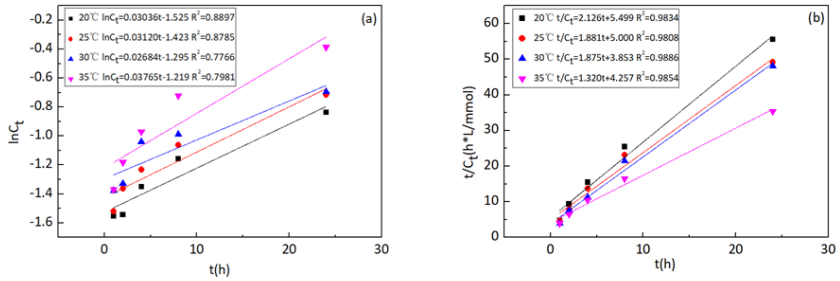

Fig. 5. Fitting of experimental data with pseudo-first-order (a) and pseudo-second-order kinetics (b).

From Fig. 5a, the plots of pseudo-first-order kinetics model at all the four temperatures have significantly deviated from the linearity with the value of R^2 lower than 0.9, indicating the non-suitability of this kinetic model. However, the fitting correlation coefficient R^2 of pseudo-second-order kinetics model are all above 0.98 (Fig. 5b), suggesting reaction order related to the concentration of the solid reactant could be affirmed as a second order reaction.

Based on Arrhenius equation[19]

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (7)$$

where k is the rate constant, A denotes frequency factor, which corresponds to the intercept of the straight line plotted by lnT against 1/T at 1/T=0. E_a is apparent activation energy, which could be obtained from the slope of the line.

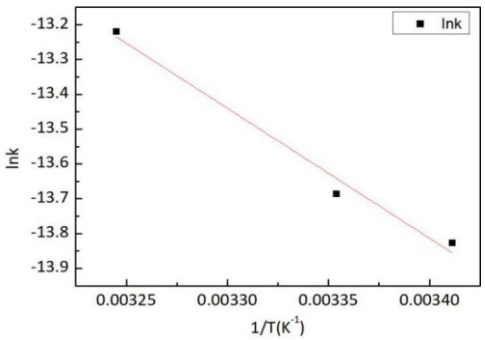

Fig. 6. Fitting of lnk with 1/T.

The Arrhenius plot was obtained based on weber–morris model, and correlation coefficient was 0.9703. Then the apparent activation energy was estimated as 31.05kJ/mol on the basis of Fig.6, indicating higher energy barrier of chromium diffusion in leather matrix.

4 Conclusions

The releasing behavior of chromium from leather was tested to simulate the surface water in this study. Our results showed that the main factors affecting Cr release from leather were temperature and contact time. The optimal leaching condition was determined as liquid-solid ratio at 20:1mL/g , rotational speed at 60rpm and deionized water was used as the fluid. However, the leachable Cr by water was low, about 0.18%-0.43% of the total chromium on the leather.

The kinetics indicated that the release rate of Cr is two type of process controlling. Weber–Morris model and pseudo-second-order kinetics model were applicable in the release of chromium from leather by water. Though the release of Cr is lasting, more than 85% leachable chromium in leather could be released in 24 h.

5 Author Contributions

[§]Liangqiong Peng and Wenjun Long contributed equally.

6 Conflict of interest

The authors of this study declare no conflict of interest.

7 Acknowledgements

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